

**DISSOLUTION KINETICS OF EVAPORITES AT PANAMINT BASIN, CALIFORNIA AND THEIR IMPLICATIONS FOR EVAPORITES ON MARS: INITIAL RESULTS.** G. R. L. Kodikara, L. J. McHenry, and T. J. Grundl, Dept. of Geosciences, University of Wisconsin- Milwaukee, Milwaukee, WI 53211, gayantha@uwm.edu, lmchenry@uwm.edu, grundl@uwm.edu.

**Introduction:** Prediction of mineral solubilities in natural waters has been a major area of research by geochemists for over 50 years (e.g. [1]). Solubility of evaporite minerals not only depends on the presence of species in solution and the activity of water, but also the environmental conditions such as temperature and pressure [2]. Calculations of mineral precipitation and solubilities based on thermodynamic data provide important constraints on geochemical systems of interest. Geochemical and numerical models have been developed to understand the formation and dissolution kinetics evaporitic minerals on Earth [3,4] and Mars [5,6]. Cyclic wetting and drying processes, especially in evaporitic playa environments, increase the complexity of predicting the evaporite mineral assemblages using geochemical data [7]. Here we present initial results of dissolution kinetic experiments on evaporite minerals from Panamint Basin, California.

**Methods:** Two 30 cm deep cores (P01 & P10) from the Panamint evaporite basin in southeastern California were collected. Field measurements were taken at each core site (temperature, pH, alkalinity) and water samples collected for laboratory analysis. Each core was divided into fifteen samples each representing 2 cm depth. Samples were air-dried and hand ground after removing organic material and sieved through 150 µm mesh. Mineral compositions were determined using X-ray diffraction (XRD). Based on mineral assemblage, five distinctive samples from each core were selected for further analysis. Three 0.200 g subsamples were placed in plastic bottles with 50 ml of distilled water, shaken, and stored at 25°C. All sample bottles were shaken daily at the same time throughout the experiment. Four 20 ml aliquots of solution were collected at weekly intervals, filtered through a 0.2 µm filter and analyzed for major cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) and anions (Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) using AA spectrophotometry and ion chromatography respectively. Bicarbonate was determined by alkalinity titration performed in the field. All laboratory water analyses were performed at the School of Freshwater Sciences, UW-Milwaukee.

Upon completion of the experiment, the remaining solids were filtered and placed on glass slides for XRD analysis. Sample P10A didn't contain solids, therefore the remaining liquid was placed on the glass slide and analyzed after all liquid was evaporated.

**Results:** Anion and cation concentrations vs. time for fluid samples extracted from 0-2 cm (P01A) and 26-28 cm (P01N) along with pH are shown in Figure 1 and 2. Na<sup>+</sup> and Ca<sup>2+</sup> reached equilibrium within a week, while others (K<sup>+</sup> and Mg<sup>2+</sup>) took longer. During the entire process, pH decreased around 1 - 2 pH units in the samples that contained the most halite and gypsum (Fig 1), while others show relatively constant pH (Fig 2). Figures 3 and 4 show the moles of cations and anions released to solution within the first week vs. depth in the core. XRD results of the P01 core reveal two distinct gypsum layers, one at the surface and another at 18-20 cm depth (Table 1), consistent with the results of the dissolution experiments (Fig 3). P10 only had one gypsum layer, at the surface (Fig. 4). Table 1 shows the mineral composition of each sample, before and after the four-week dissolution test. P10A, the surface evaporite sample, has both gypsum and halite before dissolution, but only a viscous slurry following dissolution. The remaining viscous slurry was evaporated to precipitate materials for XRD analysis, and only gypsum (no halite) was observed. One possible explanation for the NaCl disappearance the complete removal of Na<sup>+</sup> and Cl<sup>-</sup> during the early stages of dissolution. Bivariate correlation statistics for all the cation and anion measurements (200 data points) show that highest correlation (0.87) are between Na<sup>+</sup> with Cl<sup>-</sup> and Ca<sup>2+</sup> with SO<sub>4</sub><sup>2-</sup>.

Table 1. Mineral composition of each sample, identified by XRD, before and after the dissolution test.

Mineral	Dissolution	P01					P10					
		P01A	P01E	P01H	P01J	P01N	P10A	P10B	P10E	P10H	P10J	
Halite	Before	v	v	v	v	v	v	v	v	v	v	
	After	x	x	x	x	x	x	x	x	x	x	
Gypsum	Before	v	v	x	v	v	v	x	x	x	x	
	After	v	x	x	x	x	x	x	x	x	x	
Calcite	Before	x	v	v	x	x	x	v	v	v	v	
	After	x	v	v	x	x	x	v	v	v	v	
Quartz	Before	v	x	v	x	x	v	v	v	v	v	
	After	v	x	v	x	x	v	v	v	v	v	
Feldspar	Before	x	x	v	x	v	x	v	v	v	v	
	After	x	x	v	x	v	x	v	v	v	v	
Illite	Before	v	v	v	v	v	x	x	x	x	v	
	After	v	v	v	v	v	x	x	x	x	v	
Montmorillonite	Before	v	v	x	x	x	x	v	v	x	x	
	After	v	v	x	x	x	x	v	v	x	x	
Depth from the surface (cm)		0 - 2	8-10	14-16	18-20	26-28	0-2	2-4	8-10	14-16	18-20	
Present		v										
Absent		x										

**Discussion:** Based on the statistical correlations between the total released ions, XRD analysis before and after the dissolution test, and the time series analysis of dissolution (rate of the dissolution), it is clear that Na<sup>+</sup> and Cl<sup>-</sup> are released from the dissolution of halite, while Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> comes from the dissolution of gypsum. K<sup>+</sup> and Mg<sup>2+</sup> were minor compared to the dissolution of Na<sup>+</sup>, Ca<sup>+</sup>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>. These initial results show that a modern, active evaporite environment containing a

mineralogically diverse assemblage (in this case, both halite and gypsum) that is subject to seasonal flooding will dissolve and re-precipitate evaporite minerals in place. However, if subject to overland flow, the more rapidly dissolved minerals can be lost. The result would be the preferential preservation of slowly soluble phases and loss of rapidly soluble phases. These results demonstrate the importance of dissolution kinetics for the understanding of evaporite sequences in playa environments.

**Future Work:** Here we present the initial results of our dissolution experiments, and we are continuing our experiments to study and model the dissolution kinetics and thermochemistry of gypsum, halite, and other evaporite phases in this and other similar environments and their implications for past Martian environments.

**References:** [1] Garrels and Christ (1965) Solutions, minerals, and equilibria. 450p. [2] Ossorio et al. (2014) Chemical Geology, 386. 16-21. [3] Plummer et al. (1988) USGS Report. 143 p. [4] He and Morse (1993) Computers & Geosciences, 19 (1). 1-22. [5] Tosca et al. (2005) Earth and Planetary Science Letters, 240. 122-148. [6] Zolotov and Mironenko (2007) Journal of Geophysical Research, 112 (E07006). [7] Drever (1982) The geochemistry of natural waters, 388p.

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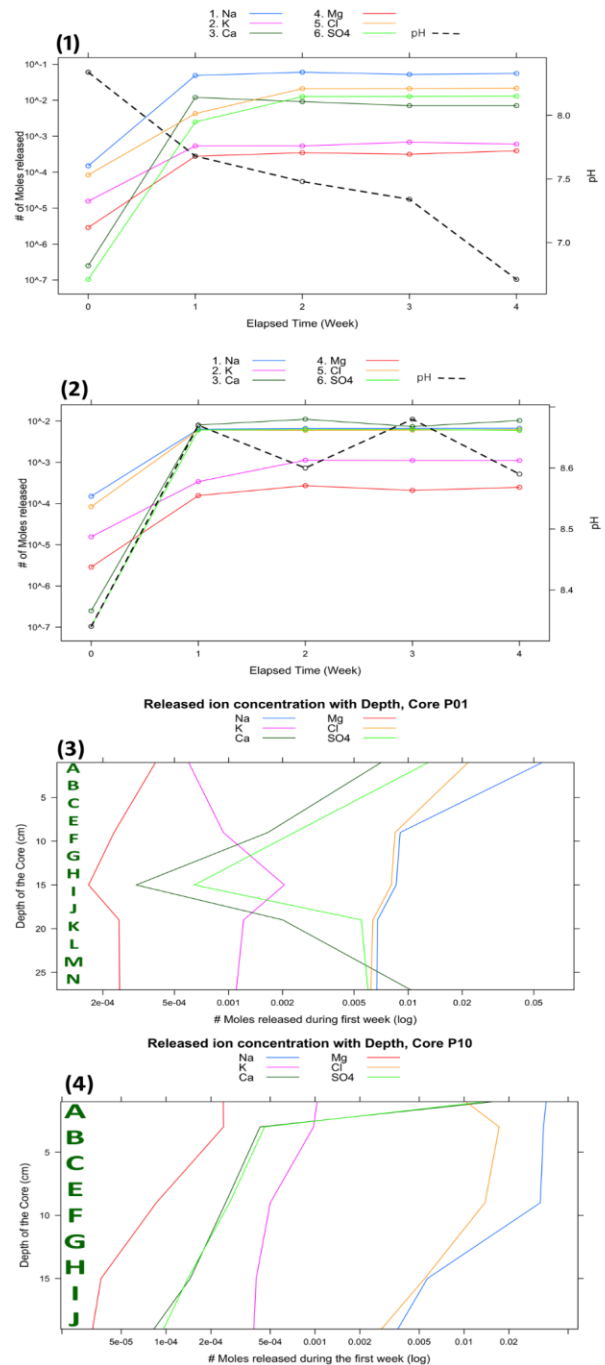


Figure 1. Quantity of dissolved cations and anions (moles) as a function of elapsed time for Core P01 surface sample, Figure 2. Quantity of dissolved cations and anions (moles) as a function of elapsed time for Core P01 sample at depth 26-28 cm, Figure 3. Ion concentrations released to the solution during the first week as a function of depth in Core P01, Figure 4. Ion concentrations released to solution during the first week as a function of depth in Core P10.